ELSEVIER

Journal of Alloys and Compounds 275–277 (1998) 209–213

Journal of ALLOYS AND COMPOUNDS

Submillimeter EPR spectroscopy of lanthanide compounds: Pair centers of Ho^{3+} in $CsCdBr_3$

B.Z. Malkin[a,*], A.I. Iskhakova[a], V.F. Tarasov[b], G.S. Shakurov[b], J. Heber[c], M. Altwein[c]

[a]*Physics Department, Kazan State University, Kazan 420008, Russian Federation*
[b]*Kazan Physical-Technical Institute, Kazan 420029, Russian Federation*
[c]*Technical University of Darmstadt, Darmstadt D-64289, Germany*

Abstract

High-frequency EPR spectra corresponding to magnetic dipole transitions between the doublet–singlet–doublet group of the lowest crystal field levels of the trigonal single ion and the symmetric dimer centers in $CsCdBr_3$ have been studied. For the dimer center, the absorption spectra in the manifold of the lowest 1024 electron-nuclear states are simulated by successive diagonalization of the electron-nuclear Hamiltonian which includes the crystal field, the electronic Zeeman energies, the magnetic and quadrupole hyperfine interactions, and the dipole–dipole interactions between the paramagnetic ions. The crystal field parameters of Ho^{3+} ions in the symmetric dimer are determined. © 1998 Elsevier Science S.A.

Keywords: Crystal field; Holmium; Hyperfine structure; Paramagnetic resonance

1. Introduction

The spectral parameters of Kramers and non-Kramers ions can be measured by submillimeter electron paramagnetic resonance (EPR) which opens the possibility of observing the hyperfine structure of transitions between crystal field levels of the ground state of a lanthanide ion [1–3]. The specific shape of the hyperfine structure and the dependence of the resonance frequencies on the magnitude and the direction of the applied magnetic field complete substantially the information obtained by site-selective optical spectroscopy. They allow us to identify unambiguously the energy levels of different optical centers and to choose the proper crystal field Hamiltonian.

In this communication, the results of experimental and theoretical investigations of the EPR spectra of dopant Ho^{3+} ions in the hexagonal double bromide $CsCdBr_3$ are summarized. They were recorded at liquid helium temperatures with backward-wave oscillators in the frequency range 160–360 GHz and for magnetic fields up to 1 T (some preliminary results have been reported in Ref. [4]). The specific feature of these crystals doped with trivalent lanthanide ions is the presence of strong positional correlations among the impurity ions. They preferentially form symmetric dimer centers of the type Ln^{3+}–Cd^{2+} vacancy–Ln^{3+} substituting for three adjacent Cd^{2+} ions in the linear chain of confacial ($CdBr_6$) octahedra [5]. These pair centers have D_{3d} symmetry. The distance between the Ln^{3+} ions attracted by the Cd^{2+} vacancy diminishes from the lattice constant $c=6.722$ Å down to 5.94 Å [5,6]. The point symmetry of the impurity site itself is C_{3v}.

In $CsCdBr_3$, the $^5I_8$ ground state of the Ho^{3+} ($4f^{10}$) ion is split predominantly by the cubic part of the crystal field (which is similar to the crystal field in elpasolite hosts [7]), resulting in a ground doublet E and the nearest triplet T_1. For centers of trigonal symmetry, the triplet state is split further into a singlet Γ_2 and a doublet Γ_3 (the energy levels are labeled by their C_{3v} group irreducible representations). The optical spectra of $CsCdBr_3$:Ho^{3+} were studied in Ref. [8] by selective laser excitation. The extensive set of energy levels has been assigned to the principal dimer center (a part of this set is given in Table 1) including the first excited singlet Γ_2 at 5.5 cm^{-1} and the doublet at 9 cm^{-1}. Due to their low excitation energies and the relatively high concentration of the pair centers, $CsCdBr_3$:Ho^{3+} crystals are suitable for studying the peculiarities of the high-frequency EPR spectra of paramagnetic dimers.

In addition to the crystal field Hamiltonian

*Corresponding author. Tel.: +7 8432 362537; fax: +7 8432 380994; e-mail: boris.malkin@ksu.ru

0925-8388/98/$19.00
PII: S0925-8388(98)00305-3